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Normal State EPR Study of the *n*-type High-T_c Superconductors

Cheol Eui Lee[1,*], W. S. Kim[1] and S. J. Noh[2]

[1]*Department of Physics, Korea University, Seoul 136-701, Korea*
[2]*Department of Physics, Dankook University, Seoul 141-210, Korea*

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Normal state EPR signals have been studied for the *n*-type high-T_c superconductors $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ and $Nd_2CuO_{3.6-x}F_{0.4-y}$. Since EPR signals were observed only in quenched non-superconducting samples and were absent in furnace-cooled samples, our results suggest that no normal state EPR signals come from pure phase *n*-type high-T_c superconductors. Our observation is consistent with previously reported absence of normal state EPR signals in the *p*-type high-T_c superconductors.

1. Introduction

Since the discovery of the high-T_c superconductors, their normal state copper EPR (electron paramagnetic resonance) signals have been a subject of much interest. In particular, the absence of the EPR signals from the Cu^{2+} ions has itself been a topic of intense interest and debate [1-4]. EPR signals have been reported in the hole-doped high-T_c superconductors below T_c, and have been interpreted as Josephson oscillations or the nonresonant microwave absorption [5-8].

The discovery of the electron-doped 24 K superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ with a negative Hall coefficient led to the term "*n*-type" (or "electron-type") high-T_c superconductors in contrast to the previously found "*p*-type" (or "hole-type") high-T_c superconductors with positive Hall coefficients [9]. Subsequently, it was found that electron-doping could also be achieved by the substitution of fluorine instead of cerium. James *et al.* found that the compound $Nd_2CuO_{3.6}F_{0.4}$ superconducts at 27 K [10]. It is the purpose of this paper to discuss EPR results of *n*-type high-T_c superconductors $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ and $Nd_2CuO_{3.6-x}F_{0.4-y}$.

2. Experiment

The samples were prepared from stoichiometric powders of Nd_2O_3, CeO_2, CuO, and CuF_2/NdF_3. The $Nd_{1.85}Ce_{0.15}$-CuO_{4-x} samples were made by 10 hours of calcination at 950°C followed by 12 hours of sintering at 1150°C. The $Nd_2CuO_{3.6-x}F_{0.4-y}$ samples were made by sintering for 14 hours at 900°C. Two different groups of samples were prepared from the same batches by distinct final cooling processes: slow furnace cooling and rapid cooling at room temperature out of the furnace (quenching). The structures were confirmed by x-ray diffraction, which showed nearly identical patterns for the quenched and the furnace cooled samples. Our choice of compositions was made for maximum superconductivity when properly annealed. The EPR spectra were taken using a Bruker EPR spectrometer in the X-band (about 9.5 GHz) sweeping the magnetic field from 0 to 1.5 T in the temperature range between 100 K and room temperature.

*Corresponding author

3. Results and Discussion

Figures 1 and 2 show the EPR spectra obtained from quenched samples of $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ and $Nd_2CuO_{3.6-x}F_{0.4-y}$ at various temperatures, respectively. They include some characteristic features that can be attributed to several different sources, comparable with signatures previously observed in R_2CuO_4 single crystals with *R*=Gd, Sm, and Eu [11]. In Fig. 1 a broad absorption structure is noticed near zero field as well as around 3000 G, which appear to be almost temperature independent. A sharp structure is also found around 400 G whose intensity increases as the temperature is lowered, indicative of a paramagnetic origin. In addition, a less pronounced structure is found around 1500 G. In Fig. 2 the most pronounced feature is the 400 G peak. Unlike in Fig. 1, EPR peaks obeying the $1/T$ dependence are also found near 800 and 1400 G. The 3000 G signature has a much broader and greater intensity than in Fig. 1 at room temperature but unlike in the cerium doped sample, it decreases as the temperature is lowered, characteristic of an antiferromagnetic correlation of the spins.

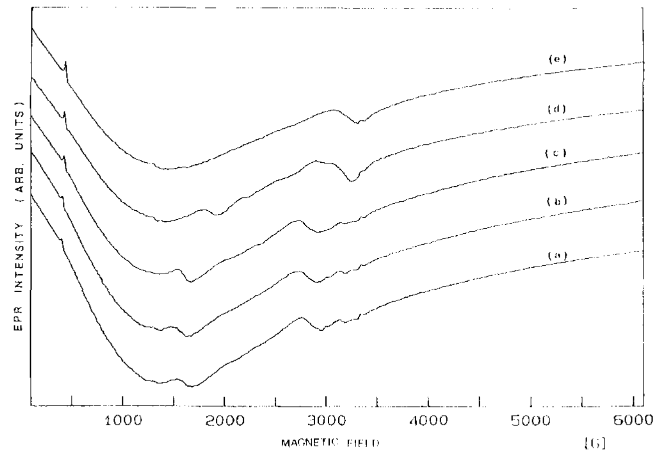

Fig. 1. EPR spectra of quenched $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ at (a) 290 K, (b) 250 K, (c) 200 K, (d) 140 K, and (e) 110 K.

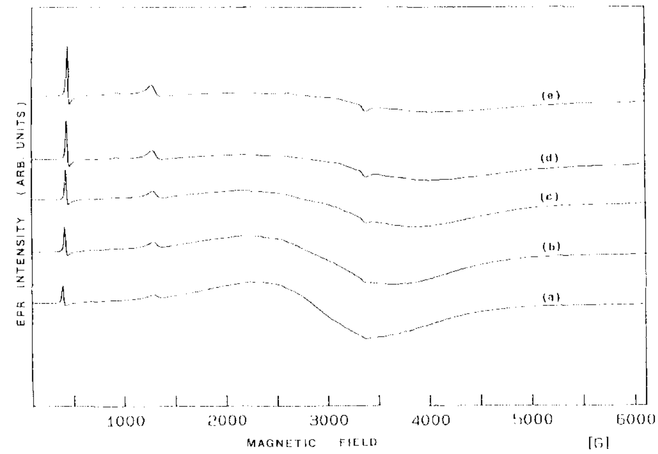

Fig. 2. EPR spectra of quenched $Nd_2CuO_{3.6-x}F_{0.4-y}$ at (a) 300 K, (b) 250 K, (c) 200 K, (d) 150 K, and (e) 110 K.

In contrast to the quenched samples, the slowly cooled samples showed no EPR signals in the temperature and magnetic field range investigated. Since superconducting samples are prepared by slow cooling, this indicates that no normal state EPR signals are observed from the n-type superconducting samples at least up to room temperature. In order to see if the cooling process indeed has anything to do with the EPR signals found from the quenched samples, we reheated and cooled them slowly. After this treatment, no EPR signals were observed, which confirms that the appearance or absence of the EPR spectra depends upon how the samples are cooled. In fact, the cooling process is generally known to dictate the oxygen stoichiometry, which appears to determine the electron states regarding the presence or absence of the EPR signals from the samples.

The absence of EPR signals in the furnace cooled samples signifies that the slow cooling process renders all the electrons into a state in which no EPR transitions are possible between the sublevels [4, 12, 13]. In normal circumstances, the spin S=1/2 state for individual unpaired electrons would not satisfy this condition. On the other hand, no transitions can take place if all the electrons are in spin S=0 paired states, which appears to be the case for the normal state high-T_c superconductors as the present work indicates.

The fact that EPR spectra are observed only in nonsuperconductive quenched samples suggests that they arise from impurity phases formed by the quenching process, and have nothing to do with the superconducting phase. In fact, it is known that quenching frequently results in phase separation in the quaternary high-T_c superconductors.

4. Conclusion

Normal state EPR studies were made on the n-type high-T_c superconductors $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ and $Nd_2CuO_{3.6-x}F_{0.4-y}$ in the present work. As a result, it was found that the EPR signals obtained from the quenched samples can be attributed to the impurity phases, while the pure superconducting phase does not show any EPR feature.

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